

# **MIDPOINT REPORT**

for the period  
17 December 1964 to 16 June 1965

## **THIN-FILM PHOTOVOLTAIC SOLAR ENERGY CONVERTERS**

by

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P. Rappaport (Project Supervisor)

Prepared for  
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

6 JULY 1965

CONTRACT NAS 3-6466

TECHNICAL MANAGEMENT  
NASA LEWIS RESEARCH CENTER  
CLEVELAND, OHIO  
SPACE POWER SYSTEMS OFFICE

RADIO CORPORATION OF AMERICA  
RCA LABORATORIES  
PRINCETON, NEW JERSEY

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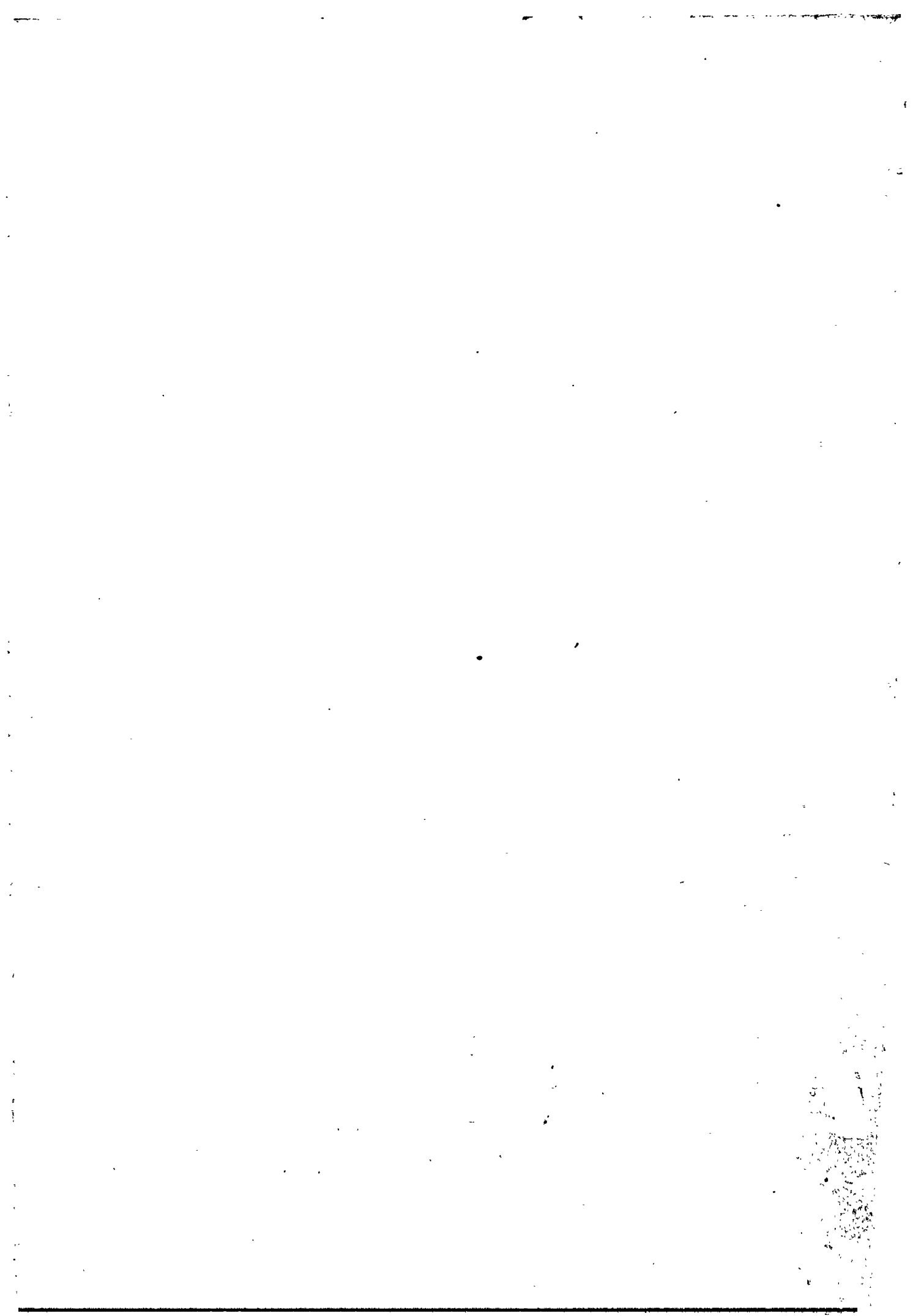
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## ABSTRACT

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By growing the multilayer structure GaAs/InAs/Al foil, the resistance through the film has been decreased and the GaAs-to-Al connection made non-rectifying. Irregularities in the properties of the Cu<sub>2</sub>Se films have been very much reduced by flash evaporating material which is carefully prepared to have a known stoichiometry. Cu<sub>2</sub>Se/GaAs/Ge-Sn/Mo cells have been made with efficiencies up to 4.6% (without an antireflection coat). They were stable in air. Cu<sub>2</sub>Se/GaAs/InAs/Al cells have been made with efficiencies up to 4%, and a measured power-to-weight ratio up to 90 watts/lb (again without an antireflection coat). With an etching treatment, cells on Al have been made which show no degradation.

*Ant-hor*



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## SUMMARY

The purpose of the program is to investigate materials and methods for the fabrication of large-area solar cells. The goals of this program are to have efficiencies higher than 5%, area capability of one foot square, flexible cells, and relatively inexpensive production costs.

By growing the multilayer structure GaAs/InAs/Al foil, the resistance through the film has been decreased and the GaAs-to-Al connection made non-rectifying. Irregularities in the properties of the Cu<sub>2</sub>Se films have been very much reduced by flash evaporating material which is carefully prepared to have a known stoichiometry. Cu<sub>2</sub>Se/GaAs/Ge-Sn/Mo cells have been made with efficiencies up to 4.6% (without an antireflection coat). They were stable in air. Cu<sub>2</sub>Se/GaAs/InAs/Al cells have been made with efficiencies up to 4%, and a measured power-to-weight ratio up to 90 watts/lb (again without an antireflection coat). With an etching treatment, cells on Al have been made which show no degradation.



## I. GaAs FILMS

### A. FILMS ON Al

Solar cells made from GaAs films on Al foil substrates appear to be an attractive structure in terms of their flexibility and light weight. At the beginning of this period we were growing GaAs films on bare aluminum substrates by the vapor transport process.<sup>1</sup> The polycrystalline GaAs films were on the order of 3/2 mil thick and the aluminum substrate was 1 mil thick. These films were characterized by a high series resistance as well as a reverse barrier when probed electrically through the film layer. It is believed that these effects arise mainly at the GaAs-aluminum interface and in the first several microns of GaAs film growth. Spectral response data showed the existence of the reverse barrier.<sup>2</sup> These effects had limited the efficiency of solar cells fabricated from these structures to about 1%.

Furthermore, after a few days, the cells would begin to degrade and the efficiency would drop below its original value. This degradation first manifested itself in an increase in the series resistance of the cell. Finally, what appeared to be a reverse barrier would begin to form and the I-V characteristic under light became indented toward the origin in the fourth quadrant. It was then discovered that a vacuum anneal of the degraded cell at about 175°C for about 30 minutes would restore the original efficiency and, in some cases, increase it over the original value. After a few days, degradation would set in again.

The principal problems connected with the GaAs/Al structure were then:

- Occurrence of high series resistance and reverse barrier in the film.
- The cell degradation problem.

Other factors such as film nonuniformity and the incidence of defects over extended areas were completely unknown quantities. As stated above, it was believed that the first problem was intimately connected with the Al-GaAs interface and the first few microns of GaAs next to it.

To better define these problem, a technique was developed to remove the Al substrate from these films, allowing electrical and optical measurements to be made on the films independent of the substrate.

To allow for both optical absorption measurements and lateral electrical measurements, the following procedure for isolating the GaAs film was used:

- (1) The sample was mounted flat on a glass slide, Al side down.
- (2) The top surface of the GaAs was polished. This was best accomplished by means of a cotton swab loaded with an alumina polishing powder of the desired fineness and rotating at a relatively slow speed (~ 300 rpm).
- (3) The sample was remounted on a glass slide by means of a transparent glue, such as Canada Balsam, with the Al side up.



- (4) The aluminum was etched off in diluted HCl, thus isolating the GaAs.

By this procedure, the exposed GaAs surface is the surface which was formerly in contact with the Al substrate. Lateral conductivity measurements were made, and the exposed surface was polished as described in step (2) above and the optical absorption spectrum was obtained. In addition, the exposed GaAs surface was etched away in a polishing etch (either  $\text{H}_2\text{O}/\text{HNO}_3/\text{HCl} = 2/1/3$ , or  $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4/\text{H}_2\text{O} = 1/18/1$ ; the etching rate was of the order of one micron per minute) and the above measurements repeated.

The results of such measurements indicate that the lateral resistance is not Ohmic, but that the current varies as

$$I = KV^n$$

where K and n are constants, I is current, and V is voltage. For all samples measured, n had a value between 1 and 2; K had values which would, at one volt, give a resistivity in the range  $10^5$  to  $10^6 \Omega\text{-cm}$ , or about  $10^3$  larger than values deduced from I-V measurements through the films. This greatly increased resistivity strongly suggests that the lateral conductivity is limited by a series of potential barriers which may be high-resistivity regions at the grain boundaries, similar to a model proposed by Petritz.<sup>3</sup> However, this model would predict a voltage-dependent conductivity only if the number of effective barriers decreased with increasing voltage. This could result if there were a distribution of barrier heights rather than a single barrier height applicable at all grain boundaries.

Upon etching off a layer of the GaAs surface, the value of n increased, and K decreased by a much greater factor than can be accounted for by the decreased thickness of the sample in almost all cases. These results are consistent with the above model if one assumes that this top layer of GaAs (formerly adjacent to the Al substrate) has a higher conductance (and smaller or fewer barriers) than the remainder of the film.

Figure 1 shows the optical absorption spectra of a GaAs film isolated from the aluminum substrate as described above. The absorption coefficient of these films is essentially identical to the single-crystal values<sup>4</sup> at wavelengths just below the band edge, but at higher wavelengths the films exhibit a residual absorption coefficient in the range 100 to  $1000 \text{ cm}^{-1}$ . Upon removing 1.1 microns of GaAs from the surface of the film (Fig. 1), there was no change in the absorption coefficient at the knee of the absorption curve, but in the region of residual absorption at higher wavelengths the absorption coefficient increased. In terms of the amount of material removed, the magnitude of the increase shown here cannot be attributed entirely to a real increase in the absorption coefficient, but must be attributed largely to uncertainties in the reflectivity correction, which introduce larger errors where the absorption coefficients are smaller.<sup>5</sup> However, almost all films show an increase in absorption coefficient in this region upon removal of the surface layer of GaAs. This would indicate that the GaAs immediately adjacent to the substrate is less absorbing in this wavelength region than the remainder of the film.

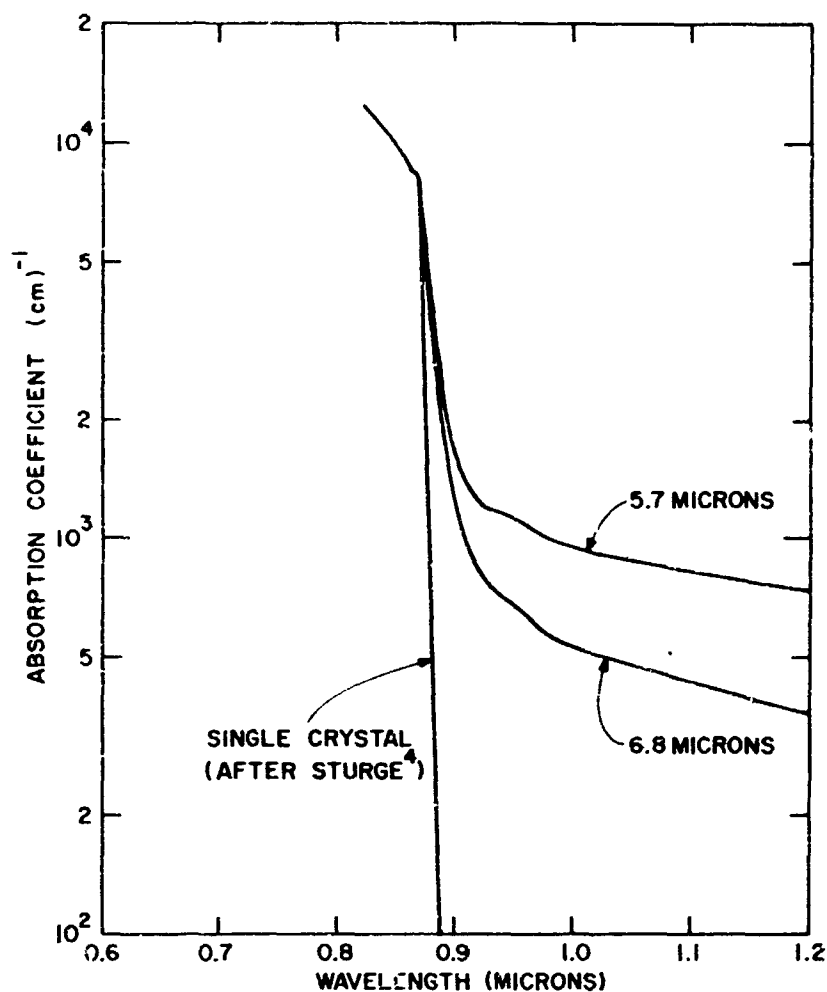


Fig. 1. Optical absorption spectra of GaAs film isolated from Al substrate.

To measure the transverse electrical characteristics of the isolated films (through the films), a slightly different procedure for mounting the films was followed. In place of the initial polishing of the top surface [steps (1) and (2) above], an Ohmic contact was applied to this surface in the following manner:

- (1) A layer of silver containing several tenths of a percent of tin was vacuum-deposited onto the top GaAs surface to a thickness such that it was essentially opaque.
- (2) The sample was then heated to a temperature of about 400 in vacuum (for a few seconds) and quickly cooled.
- (3) A layer of silver was deposited such that electrical contact was made between the alloyed region and the bare Al at the edge of the sample.
- (4) The sample was then mounted on a glass slide, Al side up, by means of red jeweler's wax.

- (5) The Al substrate was etched away as previously described, except that the Al along one edge was first masked with black wax to preserve the access to the Ohmic contact underneath.

The formation of the Ohmic contact was monitored by observing the I-V characteristics before (a) and after (b) alloying (Fig. 2). Before alloying, the curve cannot be attributed to a single barrier but is probably due to two or more opposed barriers. The observed p-on-n-type light response is attributed to the silver-GaAs barrier. After alloying, the curve is characteristic of a single n-on-p-type barrier having a poor reverse characteristic. A very weak n-on-p-type light response is also observed. These responses are attributed to the barrier at the aluminum contact, the silver-GaAs barrier having been eliminated by the alloying. There is also additional evidence for the existence of this reverse barrier first discovered by spectral response measurements.<sup>2</sup>

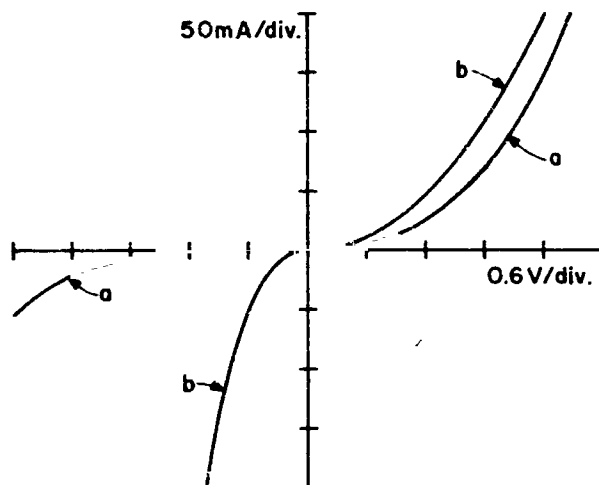


Fig. 2. I-V characteristics before and after alloying.

After mounting the samples and etching off the aluminum substrates, the I-V characteristics of the isolated films were monitored by means of a pressed gold dot (40 mil diameter) contact to the freshly exposed GaAs surface. The shape of the I-V curve at low currents (a few  $\mu$ A) was a good single-barrier characteristic indistinguishable from n-type single-crystal GaAs. However, at higher currents (a few mA) the current was still limited by resistance through the film. This resistance is comparable to that seen for the original structure on the aluminum substrate (about 100  $\Omega$ ). This series resistance was reduced upon successive removal of surface layers from the film, but the reduction was not out of proportion to the reduction of film thickness.

Using focussed microscope light, the short-circuit current was also monitored as successive layers of the GaAs were removed. Although under these conditions the short-circuit current is extremely small ( $10^{-9}$  to  $10^{-7}$  A), a consistent increase in  $I_{SC}$  was found as the film was made thinner. To obtain more quantitative measurements, these experiments were repeated using

evaporated  $\text{Cu}_2\text{Se}$  contacts to the GaAs in place of the pressed gold dots. With small  $\text{Cu}_2\text{Se}$  areas of 2.3 mm diameter, the I-V characteristics exhibit some leakage, but short-circuit currents on the order of 100  $\mu\text{A}$  were obtained with a lower-intensity light having a focussed area smaller than the  $\text{Cu}_2\text{Se}$  spots (the "standard" small light source). The results of these measurements verify those obtained with the gold dot contacts. Upon reducing the film thickness to roughly one half, both the short-circuit current and open-circuit voltage more than doubled, and, in addition, the curve shape (fill factor) improved significantly (Fig. 3).

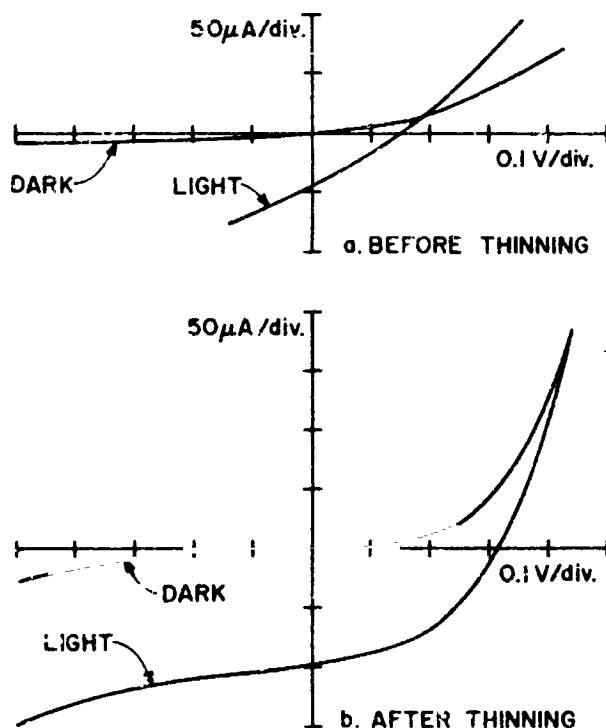


Fig. 3. Light response from film isolated from Al substrate.

The results of the measurements on the isolated films can be summarized as follows:

- (1) The photovoltaic response of the GaAs layer immediately adjacent to the aluminum substrate is poorer in all respects than that of the remainder of the film.
- (2) The layer of GaAs immediately adjacent to the substrate is more conducting (laterally) and apparently less absorbing to wavelengths above the band edge than the remainder of the film.
- (3) The lateral conductance is voltage-dependent, and may be limited by a series of barriers at the grain boundaries.
- (4) There is a high series resistance through the films which limits photovoltaic response. This property is independent of the reverse barrier at the aluminum contact, which is present in GaAs films deposited directly on aluminum.

Not much is known about any foreign materials which might form at the Al-GaAs interface which can cause potential barriers or high series resistance. Electron micrographs were taken through such films from which the aluminum substrate had been etched away in HCl. They revealed a continuous film several hundred angstroms thick which was a mixture of amorphous and tiny crystalline material. The GaAs crystallites grew on this film. Diffraction patterns could not conclusively identify the film but a similarity to  $\gamma$ -alumina was observed.

Previous experience with the molybdenum substrate led us to try various interface materials between the GaAs and aluminum to overcome some of the above-mentioned problems. Accordingly, some GaAs films were deposited onto substrates of flash-evaporated InAs on aluminum. The InAs film was n-type and on the order of several thousand angstroms thick. In addition, evaporated alloys of germanium-tin and silver-tin were tried as interface materials. None of these experiments resulted in any significant change in the film electrical characteristics.

Because of these results and of some evidence of an aluminum oxide film between the substrate and the GaAs, it was decided to investigate the effect of growing films by halide transport instead of oxide transport. Accordingly, a hydrogen chloride transport furnace was constructed for the deposition of GaAs on aluminum. The chemical reaction between the gallium and chlorine has been well investigated and will not be discussed further. In our setup, two temperature zones were established in series. GaAs chips were placed in the first zone, and they were reacted with the HCl at about 850°C. The aluminum substrate was placed in the second zone, and GaAs deposition occurred at a substrate temperature around 630°C. It was found that films could be readily grown by this arrangement. Several films were grown, but the electrical characteristics were not good. The diode characteristics were too "leaky" for solar cell application. Further modifications and investigations were planned but before they could be carried out, a structure which greatly alleviated many of the problems was devised, and the effort was concentrated on investigating it.

## B. GaAs/InAs/Al FILMS

The results obtained from the I-V characteristics, spectral response, interface materials, and studies of GaAs films with the Al substrate etched away pointed to a model of a GaAs-Al barrier and a high transverse resistance in the first few microns of the GaAs film.

The idea of trying to grow films of InAs on aluminum substrates in a manner similar to that used to grow GaAs films occurred to us. The InAs would be vapor-transported and grown to a thickness of the order of one mil. Presumably, the size of the InAs crystallites would be the same as those of GaAs when grown at the same substrate temperature (650°C). However, because of the lower band-gap of InAs (0.35 eV), it was thought that potential barriers between the InAs and aluminum would be lower than those between GaAs and aluminum. The same argument applies to the potential barriers across InAs intercrystalline boundaries. Therefore, the resistance through the InAs film should be lower. The GaAs can then be grown on top of the InAs.

If it is assumed that the growth is epitaxial, larger GaAs crystallites can be grown at any given thickness, and the first tiny (undesirable) crystallites nucleating on the aluminum can be eliminated. If this reasoning is correct, the composite film should have a lower series resistance.

Accordingly, an aluminum foil was pre-coated with a crystalline layer of n-type InAs before the growth of the GaAs film. The InAs and GaAs films were each of the order of 10 microns thick. Both were grown by vapor transport, using the oxide reaction, with a substrate temperature around 650°C and a growth rate of about 0.5 micron per hour. A schematic of the structure is shown in Fig. 4a. The resultant InAs film was n-type and, in texture, appeared similar to GaAs/Al films. The color, however, was characteristic of InAs, i.e., gray. The I-V characteristic was then observed with a pressed Au dot.

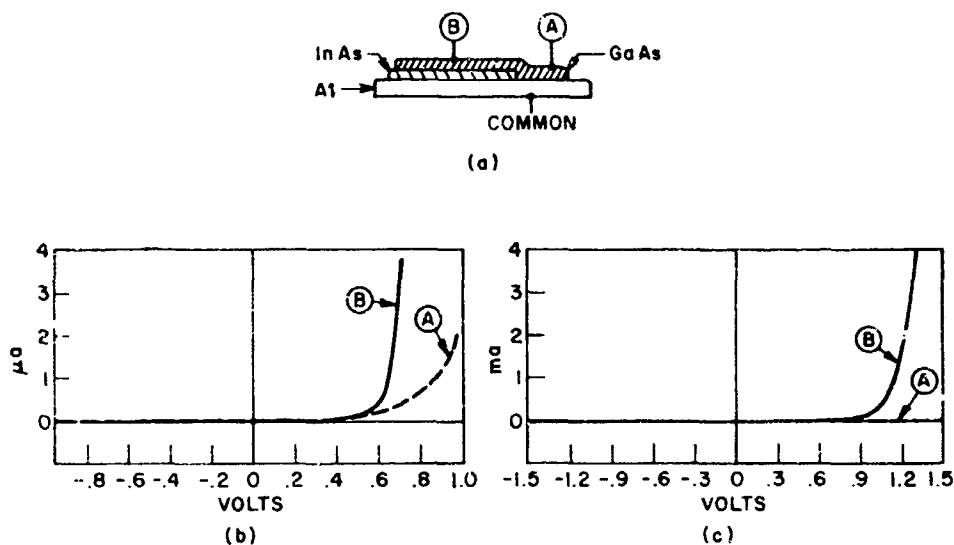


Fig. 4. Effect of InAs layer on I-V characteristics.

The resistance through the InAs itself was negligible. The characteristic (at two current ranges) through the GaAs/Al film [(A) to common, Fig. 4a] is shown in Figs. 4b and 4c. This characteristic is typical of the GaAs/Al film, and as can be seen, will not pass milliamperes at reasonable voltages. The electrical characteristics through the "double film" are shown in Fig. 4 [(B) to common]. The normal barrier is detected at the Au-GaAs but none is detected at the Al or InAs interfaces. The transverse resistance at (B) at the onset of forward conduction is on the order of 0.01 times the value measured at (A).

In addition, the spectral response showed that no reverse barrier exists in this structure. The GaAs/InAs/Al film now appears to be the base structure which seems most promising for a thin-film solar cell.

With the improved characteristics achieved with this structure, a number of films were grown and evaluated as follows:

- (1) First, the I-V characteristics are examined at random points on the film with a pressed gold dot. The pressed Au dot test provides only a limited amount of information; nevertheless, it is useful as a preliminary step for sorting the films. With this test, high-resistance films and leaky or shorted films can be eliminated from those with which we expect to fabricate "reasonable" cells.
- (2) Films which appear to have the proper I-V characteristics are then saved for  $\text{Cu}_2\text{Se}$  evaporations. These evaporations, covering specified areas from  $0.03 \text{ cm}^2$  to  $0.5 \text{ cm}^2$  (at present) then provide information about leakage and extra series resistance. Approximate solar cell characteristics of the film can also be measured, provided the optical transmission and conductivity of the  $\text{Cu}_2\text{Se}$  are known.
- (3) Finally, shelf life tests on cells are made by periodically recording the approximate maximum power out under a 3-mW tungsten lamp. The series resistance and fill factor are also observed. Between checks, the cell is kept in a plastic box with no special precautions.

The films were evaluated by this general procedure. The yield of films possessing acceptable I-V characteristics is low, about one in five.

### C. FILMS ON MOLYBDENUM

In addition to the above-described work, we continued to grow 3-mil films on Ge/Sn-coated Mo foil to provide substrates for testing  $\text{Cu}_2\text{Se}$  layers and gridding (see Section III).

At first the growth rates were quite variable. It was found that the most important factors affecting the rate were the partial pressure of water in the hydrogen and the geometrical relationship between the heating lamps and the carbon susceptor within the furnace. The hydrogen was bubbled through water at  $0^\circ\text{C}$ . This gas was allowed to flow briskly through the furnace for several hours before the temperature was raised to the growth temperature. Even so, cracking of the GaAs films and leakage due to unidentified causes limited the yield of acceptable films to about 30%.

## II. $\text{Cu}_2\text{Se}$ FILMS

At the beginning of the present period  $\text{Cu}_2\text{Se}$  films were made by the vacuum evaporation of the compound from an alumina-coated tungsten spiral. The charge was pre-heated for one minute at a higher temperature than would be used during the evaporation, then for another minute at the evaporating temperature, and then the evaporation was begun. The deposition was monitored by measuring the transmissivity of the film on glass to 1.5-eV radiation. The evaporation was usually stopped when the transmission had fallen into the range 80% to 60%.

As experience was gained with this technique, it became apparent that the sheet resistance of the films (for a given transmission) was increasing with successive evaporations at first slowly and then catastrophically. This effect seemed to show up more rapidly with the smaller charges that were used later on, when the supply of source material had been reduced.

There are corresponding changes in the optical transmission spectra. These are shown in Fig. 5. Curves 1 and 2 are for an early evaporation with a fresh charge in the boat. Curve 3 is for a resistive film made several evaporations later. Curve 1 has a shape characteristic of a degenerate single-phase material with a band-gap of about 2-1/4-eV and free carrier absorption in the infrared. Curve 3 appears to be from a completely different material showing a gradually increasing absorption constant with increasing photon energy beginning at 3/4 eV, and no evidence of free-carrier absorption.

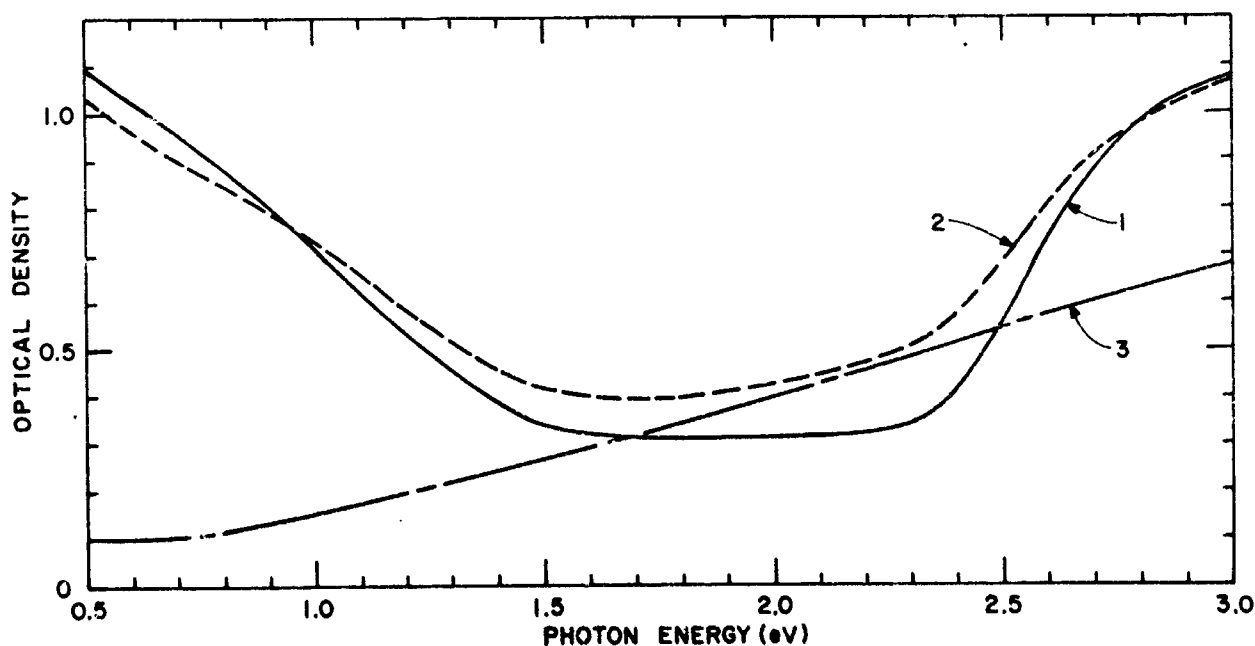


Fig. 5. Optical transmission spectra of  $\text{Cu}_2\text{Se}$  films on glass.



Cuprous selenide commonly occurs in nonstoichiometric forms,  $\text{Cu}_{2-x}\text{Se}$ , where  $x$  is as large as 0.2. It is generally believed that the copper vacancies act as acceptors and that as  $x$  increases, the material shows increasing hole concentration.\* Emission spectroscopic examination of both conducting and nonconducting films disclosed no major impurities. We concluded, tentatively, that the charge in the evaporator was changing in nonstoichiometry as the evaporations proceeded.

The flash evaporation apparatus and procedures were described previously.<sup>6</sup> This equipment was modified in two respects. The chute was provided with a radiation shield between it and the evaporator, and so far as possible the evaporator was positioned well away from the base plate, bell jar, and shields. The aim of these modifications was to reduce the heating of either the charge or deposits by radiation from the evaporator.

In use, the system was pumped to  $3 \times 10^{-6}$  torr and the evaporator out-gassed several times until the pressure had dropped to  $7 \times 10^{-7}$  torr. During the evaporation the pressure did not usually rise beyond  $3 \times 10^{-6}$  torr. The deposition was monitored by reading the resistance between two gold strips on glass, 25 mm wide and 9.5 mm apart.

After the evaporation, but before air is admitted, the resistance will generally drop slowly. This we attribute to annealing. For resistive films there is a further rapid drop in resistance on exposure to air, or a hot saturated solution of selenium in benzene. For conductive films, upon exposure to air, a slow drop in resistance continues over several days. To date we have not been able to distinguish the effects of annealing and reaction with oxygen in this slow change. In one film made from a copper-rich source  $\text{Cu}_2\text{O}$  was detected by electron diffraction.

The results of the experiments on the effect of the nonstoichiometry of the source material are given in Table I.

The following model is proposed to account for the observed resistivity changes reported above. Films which are initially close to stoichiometric composition drop in resistivity because copper is removed from them to form either the oxide or more selenide depending on the treatment. Secondly, films with compositions close to  $\text{Cu}_{1.8}\text{Se}$  are more stable in resistivity (and probably less reactive). Finally, all films come to approximately the same resistivity, if the starting material is in the range  $\text{Cu}_2\text{Se}$  to  $\text{Cu}_{1.8}\text{Se}$ .

In other experiments, Cu or  $\text{Cu}_2\text{O}$  was deliberately added to the starting material. In these cases, films were produced with permanently high resistivities which we attribute to excessive amounts of  $\text{Cu}_2\text{O}$  in the films.

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\* There are complications with thin films. Sorokin (Isz. Vysshikh Uchebn Zavednii, Fiz., No. 6, pp. 158-63, 1961, seen only in abstract) states that the resistivity is thickness-dependent at thicknesses less than 2000 Å. We disagree and believe that atmospheric oxidation influences the results. This is discussed later.

Table I  
Summary of Experiments to Determine Effect of  
Nonstoichiometry of Source Material  
(All resistances are in ohms.)

| Source Material | Source Composition | $R_{vac}$       | $R_{air}$       | $R_{treatment}$ | $R_{final}$ | $R_{70}$ |
|-----------------|--------------------|-----------------|-----------------|-----------------|-------------|----------|
| A               | $Cu_{2.01}Se$      | 8500            | 50              | -               | 24          | 48       |
|                 |                    | $2 \times 10^7$ | $1 \times 10^7$ | 1000            | 950         | 500      |
|                 |                    | 2500            | 450             | 45              | 45          | 90       |
| B               | $Cu_{1.99}Se$      | 40              | 39              | 23              | 22          | 45       |
| C               | $Cu_{1.81}Se$      | 300             | 280             | -               | -           | -        |
|                 |                    | 62              | 54              | -               | 60          | 54       |
| D               | $Cu_{1.81}Se$      | 60              | 55              | -               | 48          | 55       |

Explanation of symbols:

Samples: A - the Cu-rich end of an inhomogeneous ingot

B - the Se-rich end of the same ingot

C - a powder made by chemical precipitation; the first film broke up under chemical treatment

D - a more homogeneous ingot

Composition: as determined by chemical analysis. The films are of different, unmeasured thicknesses.

$R_{vac}$  - the resistance at the end of the evaporation

$R_{air}$  - the resistance soon after the admission of air

$R_{treatment}$  - the resistance after further exposure to air, or a hot benzene solution of selenium

$R_{final}$  - the resistance at least 5 days later

To compare the results we calculate:

$R_{70}$  - the approximate resistance of the same film when thin enough to give 70% transmission at 1.5 eV.

Finally, a series of films of different thicknesses,  $t$ , were made with sample D. If  $\alpha$  is the absorption coefficient for light,  $T$  the transmission, and  $s$  the specific resistance (assumed independent of film thickness) then

$$T \propto e^{-\alpha t}$$

and

$$\frac{1000}{R_{\text{final}}} = \frac{1000t}{s}$$

A plot of  $\ln T$  against  $1000/R_{\text{final}}$  should then yield a straight line as shown in Fig. 6. A transmission of 93% for zero film thickness represents the transmission of the bare glass.

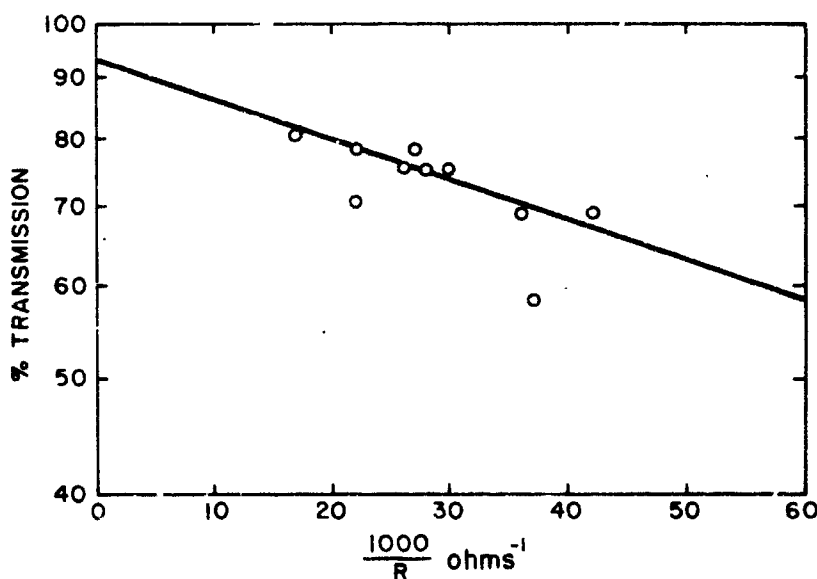


Fig. 6. Log transmission vs.  $1000/R$  for  $\text{Cu}_{1.81}\text{Se}$  films.

We conclude that in this range of thickness (of the order  $10^{-6}$  cm) and with this nonstoichiometry, the specific resistance is not a strong function of film thickness. Further, at 1.5 eV a 70% transmitting film of this composition has a sheet resistance of 73  $\Omega$  per square, which is lower than obtained in the earlier work.

Figure 7 compares the optical absorption spectra of a film made by flash evaporation with that of one made by conventional vacuum evaporation.

The suitability of a film of given sheet resistance for use in a solar cell depends on the optical absorption spectrum above 1.45 eV, and also on the nature of the barrier it forms to GaAs. The best stoichiometry and film thickness can be found most readily by making cells from  $\text{Cu}_{2-x}\text{Se}$  preparations of known stoichiometry.

Some films were also made by evaporating Cu onto glass and converting the deposit by immersion in a hot benzene solution of selenium. At first, trouble

was experienced with oxidation of the Cu film. This was very much reduced by depositing a layer of wax (benzene soluble) over it before exposure to the air. Even so, the results were inconsistent. To obtain a 70% transmitting selenide film the copper film must be much thinner than the resulting selenide film and, in fact, it was difficult to obtain the correct thickness by monitoring its resistance. There were probably other difficulties (connected with the nucleation of the Cu film) in obtaining reproducible film morphology. The attempts were discontinued when the flash-evaporation technique became available.

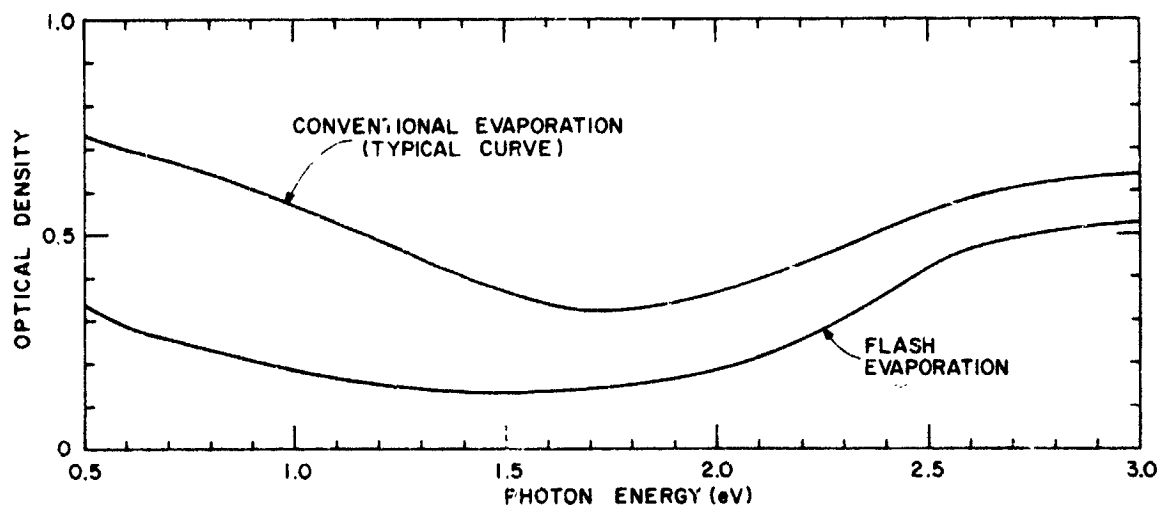


Fig. 7. Variation of optical transmission spectra with method of deposition.

Finally, it may be concluded that:

- (1) The initial method for depositing  $\text{Cu}_2\text{Se}$  gave films which exhibited a large variability in properties such as resistivity and optical absorption spectra.
- (2) These variations also appeared in the photovoltaic properties of cells made with this material. These show up primarily as variations in fill factor and open-circuit voltage which leads to corresponding variations in cell efficiency.
- (3) Reproducibility of film properties has been achieved primarily by a more careful synthesis of source material, and also by changing the method of film deposition.
- (4) Optimization of  $\text{Cu}_2\text{Se}$  film properties is expected to result when source material of appropriate nonstoichiometry is obtained.
- (5) The best sunlight efficiencies measured on cells consisting of  $\text{Cu}_2\text{Se}$  barriers on single-crystal GaAs are in the range of 5%. Since values in this same range have been obtained from cells of polycrystalline GaAs, the efficiency of polycrystalline cells is apparently not limited per se by the polycrystalline nature of the material.

### III. CELLS

#### A. CELLS ON MOLYBDENUM

As mentioned earlier, a number of cells were made on Mo to test the use of  $\text{Cu}_2\text{Se}$  layers. The cells were  $0.725 \text{ cm}^2$  in area and a closer-spaced gridding was used: four evaporated 5-mil lines, 84 mils center to center, joined by a 5-mil busbar at one end. Of 14 cells which did not show obvious leakage or short circuits, ten had efficiencies between 3% and 4%, and three had efficiencies of 4.3%, 4.4%, and 4.6%. The optimum 1.5-eV transmission for the  $\text{Cu}_2\text{Se}$  film with this gridding is close to 70%. These cells did not have an anti-reflection coating.

Some of the variability in the results originates in leakage in the GaAs films, but we now know that the  $\text{Cu}_2\text{Se}$  films were also a source of variation.

These cells were usually tested within a day of being made. When re-tested several weeks later, most showed a slight increase in efficiency. Some preliminary studies were made of the effect of vacuum annealing of "aged" cells. Twenty minutes at  $100^\circ\text{C}$  produced a slight increase in efficiency, i.e., 3.9% to 4.0%. There was a slight increase in  $V_{\text{OC}}$ . Ten minutes at  $200^\circ\text{C}$  gave a reduction in  $V_{\text{OC}}$  and efficiency. These results, while encouraging, need to be extended.

#### B. CELLS ON GaAs/InAs/Al

Small-area cells utilizing the new structure were made by evaporating  $\text{Cu}_2\text{Se}$  coating onto the GaAs. One of these cells is shown in Fig. 8a. Figure 8b shows the I-V characteristic under 3-mW illumination. This cell was further tested under the artificial sun at  $100 \text{ mW/cm}^2$  input. The open-circuit voltage was 0.46 V, the short-circuit current was 0.51 mA, and the efficiency was 4%. Note that this cell is less than 2 mils thick.

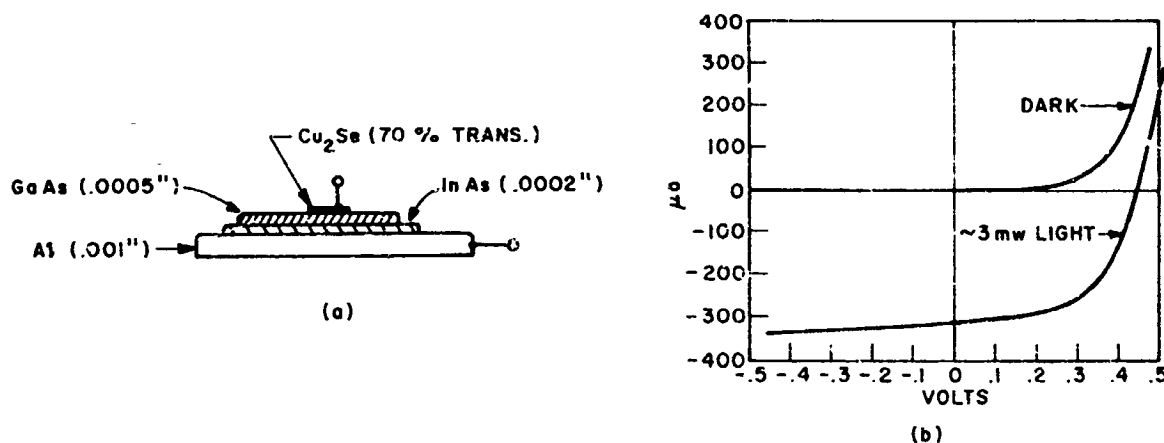


Fig. 8. Light response of  $0.03 \text{ cm}^2$  cell on aluminum.

Several other cells have been evaluated in an artificial sun at 100 mW/cm<sup>2</sup>. Their areas are between 0.03 cm<sup>2</sup> and 0.5 cm<sup>2</sup>, with an efficiency range between 2% and 4%. It is emphasized that these are approximate figures, not exact measurements.

The significance of these results is that the cell on aluminum foil can compete in efficiency with the cells made to date on Mo but at a higher power-to-weight ratio.

The maximum power outputs from two small-area cells were measured in the artificial sun at 100 mW/cm<sup>2</sup> input. The cells were then weighed. The first cell, estimated to have an efficiency around 4%, had a power-to-weight ratio of 90 W/lb. The second cell, estimated to have an efficiency of around 3%, had a power-to-weight ratio of 70 W/lb. The structure of these cells was as shown in Fig. 8a; there were no coatings, leads, or encapsulations attached. As far as we know, this is the highest power-to-weight ratio reported to date.

It has been mentioned in Section I that the cells on Al foil tended to degrade within a few days of fabrication. This is in contrast to cells made on Mo or on single-crystal GaAs which do not degrade. Further, the degradation of the cells on Al manifested itself mainly in an increase in series resistance through the cell. The original efficiency (or a higher one) could be restored with a vacuum anneal. It was found that the best annealing conditions were about 175°C for 1/2 hour. (When the annealing temperature was over 200°C, the barrier tended to become leaky and this condition could not be reversed.) In a series of exploratory experiments, the GaAs/InAs/Al films were etched with dilute nitric acid (20 parts H<sub>2</sub>O to 1 part HNO<sub>3</sub>) and so were the cells later made from them. Life tests which have gone on for about one month to date, show that no degradation has occurred. Figure 9 is a graph of the results of the shelf life tests. The cells are stored in boxes and tested

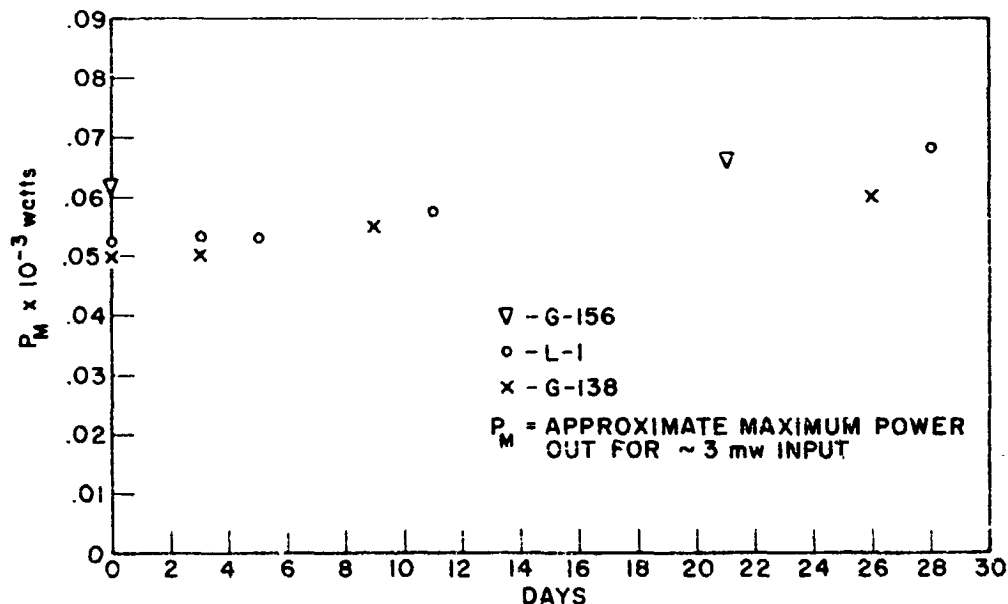


Fig. 9. Shelf life test of GaAs/InAs/Al film solar cells.

periodically as shown in the graph. It is significant that of the three cells chosen at random, none have as yet shown any degradation in the tests. The cells are bare and there are no desiccants or encapsulants present. This phenomenon is not yet understood and further etching experiments must be done to find the necessary and sufficient conditions to give stability. From the results it appears as though the dilute nitric acid is etching some substance off the GaAs film which previously had participated in a reaction which resulted in degradation.

### C. CELLS ON SINGLE-CRYSTAL GaAs

When well-conducting layers of  $\text{Cu}_2\text{Se}$  had been produced by flash evaporation it seemed of interest to try them on single-crystal GaAs.

A 78% transmitting layer (at 1.5 eV) was put onto a single crystal and gridded in the standard manner (see Section A. above). The efficiency was 5.45% with  $V_{OC} = 0.7$  V,  $I_{SC} = 11.4$  mA/cm<sup>2</sup>.

#### IV. OTHER STUDIES

A quick survey was made of other possible barrier-forming materials. The following were evaporated by electron-beam heating: molybdenum boride, niobium carbide, tantalum carbide, tantalum boride, titanium nitride, zirconium carbide, and zirconium nitride.

In general, there was evidence of decomposition. For example, with titanium nitride the pressure rose more than usual on heating, and a conducting, nearly opaque, deposit was formed. On admission of air the deposit became more transparent and also more resistive. This suggests that nitrogen was evolved on heating and that titanium was deposited and later oxidized. Since none of the deposits showed a promising combination of transparency and conductivity the matter was not pursued.

In another experiment, nickel boride was deposited by flash evaporation. Again, it was too opaque to be used at an acceptable sheet resistance.



## V. CONCLUSIONS

We conclude that cells with the structure  $\text{Cu}_{1.8}\text{Se}/\text{GaAs}/\text{InAs}/\text{Al}$  foil offer the best present approach to our objectives. The introduction of the InAs layer has eliminated the resistance through the film and removed the reverse barrier previously noticed. The introduction of flash evaporation has made the deposition of the  $\text{Cu}_{1.8}\text{Se}$  layers more reproducible.

Even without optimizing the structure and without an antireflection coat we have achieved 4% efficiency and 90 W/lb in small areas. The cells are flexible and recent cells have been stable.

## VI. ACKNOWLEDGMENTS

G. Mark and R. W. Pratt have provided technical assistance during the course of this work. We are also indebted to the Materials Analysis Group headed by S. J. Adler for supporting work in both chemical and physical analysis, and to J. J. Hanak and H. S. Berman for help with the electron-beam evaporator.

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